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(54) Title: BLENDS OF SUCROSE- AND AROMATIC AMINE INITIATED POLYETHER POLYOLS AND THEIR USE IN RIGID POLYURETHANE FOAM MANUFACTURE (57) Abstract <p>The disclosed invention relates to an isocyanate reaction system having improved capacity for solubilizing hydrocarbon blowing agents. The composition includes a sucrose based polyether polyol and an aromatic amine based polyol. In another aspect, the invention relates to a method of producing a polyurethane foam by reacting an organic polyisocyanate with the polyfunctional isocyanate-reactive composition in the presence of a hydrocarbon blowing agent.</p>		

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TITLE OF THE INVENTION

BLEND OF SUCROSE- AND AROMATIC AMINE INITIATED POLYETHER POLYOLS AND THEIR USE IN RIGID POLYURETHANE FOAM MANUFACTURE

TECHNICAL FIELD

5 The invention relates to polyol blends and polyurethane reaction systems which include these blends, especially to sucrose based polyol blends.

BACKGROUND ART

10 Rigid polyurethane foams for refrigeration appliances as well as for applications such as rigid faced panels, hot water heaters, etc. desirably employ zero ozone depleting (ODP) physical blowing agents. These zero ODP blowing agents include lower alkanes such as cyclopentane, isopentane and normal pentane.

15 The use of lower alkanes such as cyclopentane, isopentane and normal pentane as zero ODP blowing agents is limited because of the poor solubility of these alkanes and the difficulties in obtaining compatible non-separating blends of these alkanes in the polyols used to produce rigid
20 polyurethane foams.

Previous attempts to obtain compatible non-separating blends have employed more than 40% by weight aliphatic and aromatic amine based polyether polyols. Aromatic amine based polyether polyols, however, disadvantageously have high
25 viscosity, which adversely affects foam flow. Aliphatic amine based polyether polyols, however, are disadvantageously autocatalytic. Aromatic amine initiated polyols also are disadvantageously autocatalytic which limits adjustment of reactivity in applications which require slow reaction
30 profiles.

Other attempts to obtain compatible non-separating blends were directed to the use of solubilizing additives such as C₄-C₃₀ polyoxyethylene polyether monols and polyester polyols to improve solubility of lower alkanes in the polyols. The

use of solubilizing additives such as C₄-C₃₀ polyoxyethylene polyether monols and polyester polyols, however, has disadvantages such as softening of the foam matrix.

A need therefor exists for polyol blends which overcome these disadvantages.

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DISCLOSURE OF THE INVENTION

The invention relates to an isocyanate reaction system having improved capacity for solubilizing hydrocarbon blowing agents that is substantially free of solubilizing additives.

10 In a preferred aspect, the sucrose based polyol is present in an amount of about 60 wt. % to about 85% wt. % and the toluene diamine based polyol is present in an amount of about 40 wt. % to about 15 wt., all amounts based on total combined weight of the sucrose based polyol and the toluene diamine based polyol.

15 The isocyanate reaction systems of the invention include a sucrose based polyether polyol and an aromatic amine based polyol. The sucrose based polyol has a hydroxyl number of about 25 to about 700. The aromatic amine based polyether polyol is any of diaminodiphenylmethane based polyether
20 polyols, toluene diamine based polyols, and mixtures thereof, preferably toluene diamine based polyols. The diaminodiphenylmethane based polyether polyols have a hydroxyl number of about 295 to about 325 mg KOH/gram. The toluene diamine based polyols have a hydroxyl number of about 350 to
25 about 810 mg KOH/gram, and a functionality of about 3.7 to about 4.0. The hydrocarbon blowing agents may be any of cyclopentane, isopentane, n-pentane, neopentane, n-butane, cyclobutane, methylcyclobutane, isobutane, propane, cyclopropane, methylcyclopropane, n-hexane, 3-methylpentane,
30 2-methylpentane, cyclohexane, methylcyclopentane, n-heptane, 2-methylhexane, 3-ethylpentane, 2,2,3-trimethylbutane, 2,2-dimethylpentane, cycloheptane, methylcyclohexane, 2,2-dimethylbutane and 2,3-dimethylbutane. The reaction system also can include a glycerine initiated polyether polyol having

a hydroxyl value of about 53 to about 57 mg KOH/gram and a catalyst. The catalyst may be any of pentamethyldiethylenetriamine, dimethyl cyclohexyl amine, 1,3,5-tris(3-(dimethylamino)propyl) hexahydro-s-triazine, tin(II) acetate, tin(II) octanoate, tin(II) ethylhexanoate and tin(II) laurate, dibutyltin diacetate, dibutyltin dilaurate, dibutyltin maleate and dioctyltin diacetate.

In another aspect, the invention relates to an isocyanate reactive composition having improved capacity for solubilizing hydrocarbon blowing agents comprising a) a mixture containing a1) a sucrose based polyether polyol having a hydroxyl number of about 100 to about 650 mg KOH/gram and a toluene diamine based polyether polyol having a hydroxyl number of about 100 to about 600 mg KOH/gram, said sucrose based polyether polyol and toluene diamine polyether polyol being present in a ratio of about 3.75/1.0 to a ratio of about 1.55/1.0, a2) a diaminodiphenylmethane based polyether polyol, and a3) one or more low functionality polyols having functionalities from 2 to 3, b) water in an amount greater than 0.65% by weight based on the total weight of mixture a), and optionally, c) blowing agents, and d) catalysts. The sucrose based polyether polyols may have a functionality of about 4.2 to 4.8, preferably about 4.5, and the toluene diamine based polyether polyol may have a functionality of about 3.7 to about 4.0, preferably about 3.9. The compositions can also include a glycerine initiated polyether polyol having a hydroxyl number of about 45 to about 70 mg KOH/gram, preferably about 53-57 KOH/gram.

In a particularly preferred aspect, the reaction system includes about 41.0 parts of a sucrose based polyether polyol having a hydroxyl number of about 420 to about 480 mg KOH/gram, about 13.6 parts of a diaminodiphenylmethane based polyether polyol having 295 to about 325 mg KOH/gram, about 23.9 parts of a toluene diamine based polyol having a hydroxyl number of about 375 to about 405 mg KOH/gram, about 3.4 parts of a glycerine initiated polyol having a hydroxyl number of

about 53 to 57 mg KOH/gram, about 1.8 parts of a silicone surfactant, about 1.2 parts of pentamethyldiethylenetriamine, about 0.5 parts 1,3,5-tris(3-(dimethylamino)propyl) hexahydro-s-triazine, about 1.3 parts water, and about 13.3 parts cyclopentane.

5 In another aspect, the invention relates to a method of producing a polyurethane foam. The method entails reacting an organic polyisocyanate with a polyfunctional isocyanate-reactive composition described above in the presence of a hydrocarbon blowing agent.

10 MODES FOR CARRYING OUT THE INVENTION

Glossary:

- 15 1. Rubinol R 005 is a toluene diamine based polyether polyol available from Huntsman Polyurethanes. Rubinol R005 has a OH value of 330-375 mg KOH/gram.
- 20 2. Rubinol R180 is a sucrose based polyether polyol having about 70 wt. % sucrose and a hydroxyl value of 420-480 mg KOH/gram, and a functionality of 4.5 available from Huntsman Polyurethanes. The initiator used to manufacture Rubinol R180 is predominantly sucrose by weight.
- 25 3. Rubinol R145 is a diaminodiphenylmethane based polyether polyol having a hydroxyl value of 310 mg KOH/gram available from Huntsman Polyurethanes.
- 30 4. Rubinol R144 is a diaminodiphenylmethane based polyether polyol having a hydroxyl value of 295-325 mg KOH/gram available from Huntsman Polyurethanes.
- 35 5. Rubinol R159 is a diaminodiphenylmethane based polyether polyol having a hydroxyl value of 485-515 mg KOH/gram available from Huntsman Polyurethanes.
- 40 6. Rubinol R260 is a sucrose based polyether polyol having a hydroxyl value of 295-325 mg KOH/gram and a functionality of about 4.5 available from Huntsman Polyurethanes.

- 5 7. Rubinol XR124 is a 95% pure toluene diamine based polyether polyol having a functionality of 3.9 available from Huntsman Polyurethanes. Rubinol XR124 has a OH value of 375-405 mg KOH/gram.
- 10 8. Rubinol F455 is a glycerine initiated polyether polyol available from Huntsman Polyurethanes. Rubinol F455 has a hydroxyl value of 53-57 mg KOH/gram.
- 15 9. Rubinate M is polymeric methylene diphenyl diisocyanate available from Huntsman Polyurethanes.
- 20 10. Polycat 5 is pentamethyldiethylenetriamine available from Air Products and Chemicals, Inc.
- 25 11. Polycat 8 is dimethyl cyclohexyl amine from Air Products and Chemicals, Inc.
- 30 12. Polycat 41 is 1,3,5-tris(3-(dimethylamino)propyl) hexahydro-s-triazine available from Air Products and Chemicals, Inc.
- 35 13. Suprasec 5005 is polymeric methylene diphenyl diisocyanate available from Huntsman Polyurethanes.
- 40 14. Tegostab B8461 is a silicone surfactant available from Goldschmidt Chemical Corporation.
15. As used herein, substantially complete hydrocarbon solubility means no physical separation of the hydrocarbon or other ingredients normally used to make polyether polyol blends.

Sucrose based polyether polyol blend compositions

45 The polyol blends of the invention include sucrose based polyether polyol, an aromatic or aliphatic amine based polyether polyol, and a toluene diamine based polyether polyol. The blends comprise predominately sucrose based

polyether polyols. The blends also can include blowing agents, as well as optional catalysts, chain extenders, and additives.

Sucrose based polyether polyols employed in the polyol blends of the invention have hydroxyl values from about 25 mg KOH/gram to about 700 mg KOH/gram, preferably about 40 mg KOH gram to about 600 mg KOH/gram, most preferably about 420 mg KOH/gram to about 480 mg KOH/gram.

Sucrose based polyether polyols and their method of manufacture are well known in the art. These polyether polyols may be prepared by any known process such as, for example, the process disclosed by Wutz in 1859, Ulmann's Encyclopedia of Industrial Chemistry, Vol. A21, pp 670-674, VCH publishers Inc., (1992) and Encyclopedia of Chemical Technology, Vol. 7, pp. 257-262, published by Interscience Publishers, Inc. (1951), Le Maistre et al., "The Reaction of Sucrose with Ethylene Oxide," J. Org. Chem., 13, pp. 782-785 (1948), or in U.S. Pat. 4,943,649; 4,380,502; and 4,230,824.

Useful sucrose based polyether polyols are made from an initiator that includes sucrose reacted with one or more alkylene oxides. These alkoxyated sucrose polyols may contain alkoxylation products derived from other ingredients in the initiator mixture. In most cases, they contain alkoxylation products of lower molecular weight diols and triols such as diethylene glycol, glycerine and/or water. The sucrose based polyether polyols may have a functionality of about 4.2 to 4.8, preferably about 4.5. Sucrose based polyether polyols which have a functionality of about 4.2 to about 4.8 are well known in the art.

Examples of sucrose based polyether polyols which may be used include but are not limited to Rubinol R180 and Rubinol 260, preferably Rubinol R180.

Aromatic amine based polyether polyols which may be used in the invention include those made from an aromatic amine reacted with one or more alkylene oxides.

Useful aromatic amine based polyether polyols include those based on diaminodiphenylmethane ("DAPDM") and/or toluenediamine ("TDA") initiators. The alkoxyated aromatic amine polyols may contain alkoxylation products derived from other ingredients in the initiator mixture. In most cases they contain alkoxylation products of lower molecular weight diols and triols such as diethylene glycol, glycerine and/or water. In addition, the aromatic amine based polyether polyol may contain lower molecular weight diols and triols such as diethylene glycol, dipropylene glycol and/or glycerine.

Aromatic amine based polyether polyols such as TDA-based polyether polyols and diaminodiphenylmethane or polymethylene polyphenylene polyamine (DADPM)-based polyether polyols have been described as suitable isocyanate-reactive compounds for hydrocarbon blown rigid polyurethane foams (see, for example, EP 421269, WO 94/25514, EP 708127, US 5523333, US 5523332, US 5523334 and EP 617068). None of these prior art documents, however, suggests that substantially complete solubility of a hydrocarbon blowing agent can be achieved without solubilizing additives.

Examples of DADPM based polyols useful in the invention include Rubinol R 144, Rubinol R 145, and Rubinol R 159, preferably Rubinol R144.

Examples of TDA based polyols useful in the invention include but are not limited to Rubinol XR124 and Rubinol R 005, preferably Rubinol XR124.

TDA-based polyether polyols for use in the present invention generally have OH numbers in the range of about 350 to about 810, preferably about 350 to about 470 mg KOH/g, more preferably about 350 to about 430 mg KOH/g and have functionalities in the range of about 3.7 to about 4.0, preferably about 3.9. The molecular weight is generally between about 280 to about 640 g/mol. TDA-based polyether polyols having this range of functionalities and OH values are well known in the art.

TDA-based polyether polyols which may be used in the present invention are obtained by the addition of alkylene oxides, such as ethylene oxide and/or propylene oxide to one or more of the various isomers of toluene diamine such as 2,4-, 2,6-, 2,3- and 3,4-TDA. Preferably 2,3- and/or 3,4-TDA (ortho-TDA or vicinal TDA) is used as initiator with up to 25 wt% of total initiator of meta-TDA (2,4- and/or 2,6-TDA). Vicinal TDA is a pure isomer or mixture thereof, preferably containing about 20 to about 80 wt% 2,3-TDA and about 80 to about 20 wt% 3,4-TDA. Other co-initiators can be used additionally in an amount up to about 60 % by weight of total initiator, preferably between about 5 and about 10 % by weight.

Glycerine initiated polyether polyols having a hydroxyl number of about 45 to about 70 mg KOH/gram, preferably about 53-57 KOH/gram also may be included in the isocyanate reaction systems of the invention. These glycerine initiated polyether polyols are well known in the art.

Blowing agents which may be used in the blends of the invention include hydrocarbon blowing agents, preferably zero ODP blowing agents such as (cyclo)alkanes containing from 3 to 7 carbon atoms such as cyclopentane, isopentane, n-pentane, neopentane, n-butane, cyclobutane, methylcyclobutane, isobutane, propane, cyclopropane, methylcyclopropane, n-hexane, 3-methylpentane, 2-methylpentane, cyclohexane, methylcyclopentane, n-heptane, 2-methylhexane, 3-ethylpentane, 2,2,3-trimethylbutane, 2,2-dimethylpentane, cycloheptane, methylcyclohexane, 2,2-dimethylbutane and 2,3-dimethylbutane. Particularly preferred hydrocarbons are the C₅(cyclo)alkanes such as cyclopentane, n-pentane and isopentane, and any mixtures thereof.

Useful mixtures of n-pentane and isopentane include isopentane and n-pentane in a weight ratio of between about 20:80 to about 20:80. Another other useful mixture is a mixture of cyclopentane and isopentane and/or n-pentane in a

weight ratio cyclopentane:n/isopentane of between about 5 to about 80 wherein the weight ratio n-pentane:isopentane is between about 20:80 to about 80:20.

In addition to the hydrocarbon blowing agent(s), other physical blowing agents may be used in amounts up to about 80 wt. % of the total physical blowing agents present.

Suitable other physical blowing agents include those well known and described in the art, for example dialkyl ethers, alkyl alkanoates, aliphatic and cycloaliphatic hydrofluorocarbons, hydrochlorofluorocarbons, chlorofluorocarbons, hydrochlorocarbons and fluorine-containing ethers, water and carbon dioxide.

Generally water or other carbon dioxide-evolving compounds are used together with the physical blowing agents. Where water is used as a chemical co-blowing agent, water is present in an amount of up to about 5%, preferably up to about 3% by weight based on the isocyanate-reactive compound.

The total amount of blowing agent used in the polyol blends of the invention for producing polyurethane foams can be readily determined by those skilled in the art, but typically is from about 10 to about 50, preferably about 20 to about 40 % by weight based on the total reaction system.

In the case of blowing with solely cyclopentane as hydrocarbon, the amount of sucrose based polyol is preferably about 20 to about 80 % by weight, more preferably about 40 to about 75 % by weight, most preferably about 50 to about 62%, the amount of TDA-based polyether polyol is preferably about 5 to about 40 % by weight, more preferably about 10 to about 40 % by weight, most preferably about 13 to about 35 %, and the amount of DADPM-based polyol is preferably about 4 to about 50 % by weight, more preferably about 10 to about 30% by weight, most preferably about 12 to about 20 %, all amounts by weight based on total weight of isocyanate-reactive compounds.

Catalysts used for producing the polyurethane rigid foams are, in particular, compounds which strongly accelerate the

reaction hydroxyl groups, with the organic, modified or unmodified polyisocyanates. Suitable catalyst compounds are strongly basic amines. Examples which may be mentioned are pentamethyldiethylenetriamine, dimethyl cyclohexyl amine, 1,3,5-tris(3-(dimethylamino)propyl) hexahydro-s-triazine, amidines such as 2,3-dimethyl-3,4,5,6-tetrahydropyrimidine, tertiary amines such as triethylamine, tributylamine, dimethylbenzylamine, N-methylmorpholine, -ethylmorpholine, N-cyclohexylmorpholine, N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetramethylbutanediamine, N,N,N',N'-tetramethylhexane-1,6-diamine, pentamethyldiethylenetriamine, bis(dimethylamino)ethyl ether, dimethylcyclohexylamine, bis(dimethylaminopropyl)urea, dimethylpiperazine, 1,2-dimethylimidazole, and alkanolamine compounds such as triethanolamine, triisopropanolamine, N-methyldiethanolamine and N-ethyldiethanolamine and dimethylethanolamine, and 1,3,5-tris(3-(dimethylamino)propyl) hexahydro-s-triazine, and organometallic compounds such as organostannic compounds such as tin(II) salts of organic carboxylic acids, e.g. tin(II) acetate, tin(II) octanoate, tin(II) ethylhexanoate and tin(II) laurate, and the dialkyltin(IV) salts of organic carboxylic acids, e.g. dibutyltin diacetate, dibutyltin dilaurate, dibutyltin maleate and dioctyltin diacetate. The catalysts can be used either alone or in combination.

Other suitable catalysts are tris(dialkylaminoalkyl)-s-hexahydrotriazines, in particular tris(N,N-dimethylaminopropyl)-s-hexahydrotriazine, tetraalkylammonium hydroxides such as tetramethylammonium hydroxide, alkali metal hydroxides such as sodium hydroxide and alkali metal alkoxides such as sodium methoxide and potassium isopropoxide, and also alkali metal salts of long-chain fatty acids having from 10 to 20 carbon atoms, with or without lateral OH groups. Preference is given to using from about 0.001 to about 5% by weight, in particular from about 0.05 to about 2% by weight, of catalyst

or catalyst combination, based on the weight of the polyol blend.

Chain extenders and/or crosslinkers used which may be are diols and/or triols having molecular weights less than about 246, preferably from about 62 to about 174. Examples are
5 aliphatic, cycloaliphatic and/or araliphatic diols having from 2 to 14, preferably from 2 to 10 carbon atoms, such as ethylene glycol, 1,3-propanediol, 1,10-decanediol, o-, m-, p-dihydroxycyclohexane, diethylene glycol, dipropylene glycol and preferably 1,4-butanediol, 1,6-hexanediol and bis(2-
10 hydroxyethyl)hydroquinone, triols such as 1,2,4-, 1,3,5-trihydroxycyclohexane, glycerol and trimethylolpropane, and low molecular weight hydroxyl-containing polyalkylene oxides based on ethylene and/or 1,2-propylene oxide and the abovementioned diols and/or triols as initiator molecules.

15 Additives also may be included in the polyol blends. These optional additives include crosslinking agents, for example low molecular weight polyols such as triethanolamine, foam-stabilizing agents or surfactants, for example siloxane-oxyalkylene copolymers, urethane catalysts, for example tin
20 compounds such as stannous octoate or dibutyltin dilaurate or tertiary amines such as dimethylcyclohexylamine or triethylene diamine, fire retardants, for example halogenated alkyl phosphates such as tris chloropropyl phosphate, and fillers such as carbon black. Other useful additives include surface-
25 active substances, foam stabilizers, cell regulators, fillers, dyes, pigments, flameproofing agents, hydrolysis inhibitors, fungistatic and bacteriostatic substances.

Suitable surface-active substances are, for example, compounds which aid the homogenization of the starting
30 materials and may also be suitable for regulating the cell structure of the plastics. Examples include emulsifiers such as the sodium salts of castor oil sulfates or of fatty acids, and also fatty acid salts with amines, e.g. diethylamine oleate, diethanolamine stearate, diethanolamine ricinoleate,

salts of sulfonic acids, e.g. alkali metal or ammonium salts of dodecylbenzenedisulfonic or dinaphthylmethanedisulfonic acid and ricinoleic acid; foam stabilizers such as siloxane-oxyalkylene copolymers and other organopolysiloxanes, ethoxylated alkylphenols, ethoxylated fatty alcohols, paraffin oils, castor oil or ricinoleic esters, Turkey Red oil and peanut oil, and cell regulators such as paraffins, fatty alcohols and dimethylpolysiloxanes. Other substances for improving the emulsifying action, the cell structure and/or the stabilization of the foam are the above described oligomeric acrylates having polyoxyalkylene and fluoroalkane radicals as side groups. The surface-active substances are usually used in amounts of from 0 to about 2.5 parts by weight, based on 100 parts by weight of the polyol blend.

In a preferred aspect, the sucrose based polyether polyol blends of the invention include about 41% to about 62%, preferably about 41 to about 44% Rubinol R180, about 10% to about 20%, preferably about 10 to about 14% Rubinol R144, about 13% to about 35%, preferably about 20 to about 25% Rubinol XR124, and from 0% to about 5% Rubinol F455, preferably 0 to about 4% Rubinol F455, all amounts in terms of weight percent based on the total weight of the polyether polyol blend.

A preferred polyether polyol blend includes about 50% Rubinol R180, about 16.6% Rubinol R144, about 29.2% Rubinol XR124 and about 4.2% Rubinol F455, all amounts based on the total weight of the blend. More preferably, the polyether blend includes Rubinol R180 in an amount of about 41 to about 43.8%, Rubinol R144 in an amount of about 10.2 to about 14.5%, Rubinol XR 124 in an amount of about 20 to about 25.1%, Rubinol F455 in an amount of up to about 3.6%, Tegostab B 8461 in an amount of about 1.8%, Polycat 5 in an amount of about 1.2%, Polycat 41 in an amount of about 0.5%, water in an amount of about 1.3%, and cyclopentane in an amount of about

13.3%, all amounts based on the weight of the polyol blend including the cyclopentane.

The polyether polyol blends of the invention may also include non-sucrose based polyether polyols. Non-sucrose based polyols can be included in amounts of up to about 49% based on the total weight of the polyether polyol blend. Examples of non-sucrose based polyols include polyols initiated by sorbitol, glycerol, DETA, phenol formaldehyde, and mannich base.

The polyol blends of the invention advantageously achieve substantially complete solubility of zero ODP hydrocarbon blowing agents with substantially no solubilizing additives as required in the prior art. By substantially no solubilizing additives, I mean that solubilizing additives may be present in an amount less than about 1% by weight of the total polyurethane formulation.

Manufacture of Sucrose based polyether polyol blends

The hydrocarbon soluble sucrose based polyol blends of the invention are prepared by mixing together in any order of addition of the individual components of the blend.

The invention is further illustrated by reference to the following non-limiting examples.

Examples 1-9

In examples 1-9, the components shown in Table 1 are blended. All amounts are parts by weight. The appearance of the resulting polyol blend is also shown.

Table 1

Example/ Component	1	2	3	4	5	6	7	8	9
Rubinol R180	81.9	57.9	54.4	50.8	47.3	43.8	43.0	42.8	41.0
Rubinol R144	0.0	19.2	18.0	16.9	15.7	14.5	10.2	14.2	13.6
Rubinol XR124	0.0	0.0	5.0	10.0	15.0	20.0	25.1	24.9	23.9
Rubinol F455	0.0	4.8	4.5	4.2	3.9	3.6	3.6	0.0	3.4
Tegostab B8461	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
Polycat 5	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Polycat 41	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Water	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3
Cyclopentane	13.3	13.3	13.3	13.3	13.3	13.3	13.3	13.3	13.3
Appearance (1)	SEP	SEP	SEP	CLR	CLR	CLR	CLR	CLR	CLR

(1) Appearance

SEP = Mixture phase separates into more than one layer within 72 hours at room temperature

CLR = Clear solution which does not separate after 72 hours

Manufacture of Polyurethane Foams

The amounts of polyisocyanate and the polyol blends of the invention to be reacted to form a polyurethane foam, preferably a rigid polyurethane foam, depend upon the rigid polyurethane or urethane-modified polyisocyanurate foam to be produced and can be readily determined by those skilled in the art.

In operating the process for making rigid polyurethane foams which employ the polyol blends of the invention, the known one-shot, prepolymer or semi-prepolymer techniques may be used together with conventional mixing methods. The rigid foam may be produced in the form of slabstock, molding, cavity fillings, sprayed foam, frothed foam or laminates with other materials such as hardboard, plasterboard, plastics, paper or metal.

The invention thus can produce polyurethane rigid foams by reacting a sucrose based polyol blend with polyisocyanate. The sucrose polyol blend includes a sucrose based polyol and an amine based polyol wherein the sucrose based polyol is a

predominate amount by weight of the blend. As described above, the blend can include blowing agents, and also may include catalysts, additives, and, optional low molecular weight chain extenders and/or crosslinkers. If chain extenders, crosslinkers or mixtures thereof are included in the polyol blends for use in manufacture of polyurethane rigid foams, these are used in an amount of from 0 to about 30 % by weight, preferably from 0 to about 5 % by weight, based on the weight of the polyol compound

Isocyanates which may be reacted with the polyol blends of the invention to produce polyurethanes include any of those known in the art for the preparation of rigid polyurethane or urethane-modified polyisocyanurate foams, and in particular the aromatic polyisocyanates such as diphenylmethane diisocyanate in the form of its 2,4'-, 2,2'- and 4,4'-isomers and mixtures thereof, the mixtures of diphenylmethane diisocyanates (MDI) and oligomers thereof known in the art as "crude" or polymeric MDI (polymethylene polyphenylene polyisocyanates) having an isocyanate functionality of greater than 2, toluene diisocyanate in the form of its 2,4- and 2,6-isomers and mixtures thereof, 1,5-naphthalene diisocyanate and 1,4-diisocyanatobenzene. Other organic polyisocyanates which may be mentioned include the aliphatic diisocyanates such as isophorone diisocyanate, 1,6-diisocyanatohexane and 4,4'-diisocyanatodicyclohexylmethane.

Suitable organic polyisocyanates are the aliphatic, cycloaliphatic, araliphatic and preferably aromatic polyfunctional isocyanates known per se. Specific examples are: alkylene diisocyanates having from 4 to 12 carbon atoms in the alkylene radical, for example 1,12-dodecane diisocyanate, 2-ethyltetramethylene 1,4-diisocyanate, 2-methylpentamethylene, 1,5-diisocyanate, tetramethylene 1,4-diisocyanate and preferably hexamethylene 1,6-diisocyanate; cycloaliphatic diisocyanates such as cyclohexane 1,3-diisocyanate and 1,4-diisocyanate and also any mixtures of these isomers, 1-isocyanato-3,3,5-trimethyl-5-

isocyanatomethylcyclohexane (isophorone diisocyanate), 2,4- and 2,6-hexahydrotoluene diisocyanate and also the corresponding isomer mixtures, 4,4'-, 2,2'- and 2,4'-dicyclohexylmethane diisocyanate and also the corresponding isomer mixtures, and preferably aromatic diisocyanates and polyisocyanates such as 2,4- and 2,6-toluene diisocyanate and the corresponding isomer mixtures, 4,4'-, 2,4'- and 2,2'-diphenylmethane diisocyanate and the corresponding isomer mixtures, mixtures of 4,4'- and 2,4'-diphenylmethane diisocyanates, polyphenyl-polymethylene polyisocyanates, mixtures of 4,4'-, 2,4'- and 2,2'-diphenylmethane diisocyanates and polyphenyl-polymethylene polyisocyanates (raw MDI) and mixtures of raw MDI and toluene diisocyanates. The organic diisocyanates and polyisocyanates can be used either individually or in the form of their mixture.

Frequently, use is also made of modified polyfunctional isocyanates, i.e. products which are obtained by chemical reaction of organic diisocyanates and/or polyisocyanates. Examples which may be mentioned are diisocyanates and/or polyisocyanates containing ester, urea, biuret, allophanate, carbodiimide isocyanurate, uretdione and/or urethane groups. Specific examples are: organic, preferably aromatic, polyisocyanates containing urethane groups and from about 33.6 to about 15% by weight, preferably from about 31 to about 21% by weight, of NCO based on the total weight, for example 4,4'-diphenylmethane diisocyanate modified with low molecular weight diols, triols, dialkylene glycols, trialkylene glycols or polyoxyalkylene glycols having molecular weights of up to about 1500, modified 4,4'- and 2,4'-diphenylmethane diisocyanate mixtures, or modified raw MDI or 2,4- or 2,6-toluene diisocyanate, with examples of dialkylene or polyoxyalkylene glycols, which can be used either individually or as mixtures, being: diethylene and dipropylene glycols, polyoxyethylene, polyoxypropylene and polyoxypropylene-polyoxyethylene glycols, triols and/or tetrols. Also suitable are NCO-containing prepolymers containing from about 25 to

about 3.5% by weight, preferably from about 21 to about 14% by weight of NCO based on the total weight, prepared from the polyester-polyols and/or preferably polyether-polyols described below and 4,4'-diphenylmethane diisocyanate, mixtures of 2,4'- and 4,4'- diphenylmethane diisocyanate, 2,4- and/or 2,6-toluene diisocyanates or raw MDI. Other compounds which have been found to be suitable are liquid polyisocyanates containing carbodiimide groups and/or isocyanurate rings and from 33.6 to 15% by weight, preferably from 31 to 21% by weight, of NCO, based on the total weight, e.g. based on 4,4'-, 2,4'- and/or 2,2'-diphenylmethane diisocyanate and/or 2,4- and/or 2,6-toluene diisocyanate.

The modified polyisocyanates can, if desired, be mixed with one another or with unmodified organic polyisocyanates such as 2,4'-, 4,4'-diphenylmethane diisocyanate, raw MDI, 2,4- and/or 2,6-toluene diisocyanates. Organic polyisocyanates which have been found to be particularly useful and are therefore preferably used are: mixtures of toluene diisocyanates and raw MDI or mixtures of modified organic polyisocyanates containing urethane groups and from about 33.6 to about 15% by weight of NCO, in particular those based on toluene diisocyanates, 4,4'-diphenylmethane diisocyanate, diphenylmethane diisocyanate isomer mixtures or raw MDI and, in particular, raw MDI containing from 30 to 80% by weight, preferably from about 30 to about 55% by weight, of diphenylmethane diisocyanate isomers.

The polyurethane rigid foams can be produced with or without use of chain extenders and/or crosslinkers. However, the addition of chain extenders, crosslinkers or, if desired, can be advantageous for modifying the mechanical properties, e.g. hardness.

The polyurethane rigid foams are advantageously produced by the one-shot method, for example by means of the high-pressure or low-pressure technique in open and/or closed molds. It is particularly advantageously to react the polyol blend with the organic polyisocyanates or modified polyisocyanates.

The polyurethane rigid foams produced by the process of the invention have an in-place density of from about 2.0 lb/ft³ and a thermal conductivity of about 0.14 BTU•in•h⁻¹•°F•ft⁻². They are particularly suitable as insulation material in the building and refrigeration appliance sector, for example as intermediate layer in sandwich elements or for filling housings of refrigerators and freezer chests with foam.

Examples 10-13:

Examples 10-13 in Table 2 illustrate the use of the polyol blends of the invention in the manufacture of polyurethane foams by the well known pour in place or hand mix processes. The blends of Examples 10-13 are miscible.

In Table 2, Rubinol R180, Rubinol R144, Rubinol XR124, Rubinol F455, Tegostab B8461, Polycat 5, Polycat 41, water and cyclopentane are blended to produce polyol blends. All amounts are parts by weight. The polyol blends are reaction injection molded with isocyanates such as Rubinate M and Suprasec 5005 to produce reaction injection molded polyurethane.

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Table 2

Example/component	10	11	12	13
Rubinol R180	41.0	41.0	41.0	41.0
Rubinol R144	13.6	13.6	13.5	13.6
Rubinol XR124	23.9	23.9	23.7	23.8
Rubinol F455	3.4	3.4	3.4	3.4
Tegostab B8461	1.8	1.8	1.8	1.8
Polycat 5	1.2	1.2	0.4	1.2
Polycat 8	0.0	0.0	2.0	0.0
Polycat 41	0.5	0.5	0.0	0.5
Water	1.3	1.3	1.3	1.3
Cyclopentane (Tech.)	13.3	13.3	13.3	13.3
Rubinate M	103.8	0.0	0.0	0.0
Suprasec 5005	0.0	106.1	105.2	122.8
NCO/OH Index	1.08	1.08	1.08	1.23
Polyol/Isocyanate Ratio	0.963	0.942	0.951	0.814
Volume of Total Blowing agent in foam, ml/g	30.1	29.7	29.5	29.5
Polyol Temp. °F	70.0	70.0	70.0	70.0
Isocyanate Temp. °F	70.0	70.0	70.0	70.0
Polyol Pressure, psi	2000.0	2000.0	2000.0	2000.0
Isocyanate Pressure, psi	2000.0	2000.0	2000.0	2000.0
Polyol Orifice, mm	2.0	2.0	2.0	2.0
Isocyanate Orifice, mm	2.0	2.0	2.0	2.0
Thermal Conductivity, Btu-in./hr.-°F ft. ²				
75°F (55/95)	0.144	0.144	0.148	0.148
50°F (32/68)	0.142	0.140	0.140	0.145

Claims:

1. An isocyanate reaction system having improved capacity for solubilizing a hydrocarbon blowing agent comprising
a sucrose based polyether polyol having a hydroxyl number
of about 25 to about 700, and an aromatic amine based polyol
5 selected from the group consisting of diaminodiphenylmethane
based polyether polyols, toluene diamine based polyols, and
mixtures thereof,
wherein the reaction system is substantially free of
solubilizing additives.

2. The reaction system of claim 1 wherein the aromatic amine
based polyol is toluene diamine based polyol, and wherein the
sucrose based polyol is present in an amount of 60 wt. % to
about 85 wt. %, and the toluene diamine based polyol is
15 present in an amount of about 40 wt. % to about 15 wt. %, all
amounts based on total combined weight of the sucrose based
polyol and the toluene diamine based polyol.

3. The reaction system of claim 2 wherein the
20 diaminodiphenylmethane based polyether polyols have a hydroxyl
number of about 295 to about 325 mg KOH/gram, and the toluene
diamine based polyols have a hydroxyl number of about 350 to
about 810 mg KOH/gram and a functionality of about 3.7 to
about 4.0.

4. The reaction system of claim 1 further comprising a
hydrocarbon blowing agent selected from the group consisting
of cyclopentane, isopentane, n-pentane, neopentane, n-butane,
cyclobutane, methylcyclobutane, isobutane, propane,
30 cyclopropane, methylcyclopropane, n-hexane, 3-methylpentane,
2-methylpentane, cyclohexane, methylcyclopentane, n-heptane,
2-methylhexane, 3-ethylpentane, 2,2,3-trimethylbutane, 2,2-
dimethylpentane, cycloheptane, methylcyclohexane, 2,2-
dimethylbutane and 2,3-dimethylbutane.

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5. The reaction system of claim 4 wherein the hydrocarbon blowing agent is selected from the group consisting of cyclopentane, isopentane, n-pentane and mixtures thereof.

6. The reaction system of claim 1 further comprising a glycerine initiated polyether polyol having a hydroxyl value of about 53 to about 57 mg KOH/gram.

7. The reaction system of claim 1 wherein the amount of sucrose based polyol is about 50 to about 62% by weight, the amount of toluene diamine based polyether polyol is about 13 to about 35 % by weight, and the amount of diaminodiphenylmethane based polyol is about 12 to about 20 %, all amounts by weight based on total weight of isocyanate-reactive compounds, and the blowing agent is cyclopentane.

8. The reaction system of claim 4 further comprising a physical blowing agent selected from the group consisting of dialkyl ethers, alkyl alkanoates, aliphatic hydrofluorocarbons, cycloaliphatic hydrofluorocarbons, hydrochlorofluorocarbons, chlorofluorocarbons, hydrochlorocarbons, fluorine-containing ethers, water and carbon dioxide.

9. The reaction system of claim 4 further comprising a catalyst selected from the group consisting of pentamethyldiethylenetriamine, dimethyl cyclohexyl amine, 1,3,5-tris(3-(dimethylamino)propyl) hexahydro-s-triazine, tin(II) acetate, tin(II) octanoate, tin(II) ethylhexanoate and tin(II) laurate, dibutyltin diacetate, dibutyltin dilaurate, dibutyltin maleate and dioctyltin diacetate.

10. An isocyanate reaction system having improved capacity for solubilizing a hydrocarbon blowing agent comprising

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about 41.0 parts of a sucrose based polyether polyol having a hydroxyl number of about 420 to about 480 mg KOH/gram,

about 13.6 parts of a diaminodiphenylmethane based polyether polyol having 295 to about 325 mg KOH/gram,

5 about 23.9 parts of a toluene diamine based polyol having a hydroxyl number of about 375 to about 405 mg KOH/gram,

about 3.4 parts of a glycerine initiated polyol having a hydroxyl number of about 53 to 57 mg KOH/gram,

10 about 1.8 parts of a silicone surfactant,
about 1.2 parts of pentamethyldiethylenetriamine,
about 0.5 parts 1,3,5-tris(3-(dimethylamino)propyl) hexahydro-s-triazine,

about 1.3 parts water, and

about 13.3 parts cyclopentane.

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11. A method of producing a polyurethane foam comprising reacting an organic polyisocyanate with a polyfunctional isocyanate-reaction system in the presence of a hydrocarbon blowing agent, the polyfunctional isocyanate-reaction system comprising

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a sucrose based polyether polyol having a hydroxyl number of about 25 to about 700, and

25 an aromatic amine based polyether polyol selected from the group consisting of diaminodiphenylmethane based polyether polyols, toluene diamine based polyols, and mixtures thereof,

wherein the isocyanate reaction system is substantially free of solubilizing additives.

30 12. The method of claim 11 wherein the aromatic amine based polyol is toluene diamine based polyol, and wherein the sucrose based polyol is present in an amount of 60 wt. % to about 85 wt. %, and the toluene diamine based polyol is present in an amount of about 40 wt. % to about 15 wt. %, all amounts based on total combined weight of the sucrose based
35 polyol and the toluene diamine based polyol.

13. The method of claim 11 wherein the diaminodiphenylmethane based polyether polyols have a hydroxyl number of about 295 to about 325 mg KOH/gram, and the toluene diamine based polyols have a hydroxyl number of about 350 to about 810 mg KOH/gram, and a functionality of about 3.7 to about 4.0.

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14. The method of claim 11 further comprising a hydrocarbon blowing agent selected from the group consisting of cyclopentane, isopentane, n-pentane, neopentane, n-butane, cyclobutane, methylcyclobutane, isobutane, propane, cyclopropane, methylcyclopropane, n-hexane, 3-methylpentane, 2-methylpentane, cyclohexane, methylcyclopentane, n-heptane, 2-methylhexane, 3-ethylpentane, 2,2,3-trimethylbutane, 2,2-dimethylpentane, cycloheptane, methylcyclohexane, 2,2-dimethylbutane and 2,3-dimethylbutane.

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15. The method of claim 14 wherein the hydrocarbon blowing agent is selected from the group consisting of cyclopentane, isopentane, n-pentane and mixtures thereof.

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16. The method of claim 11 further comprising a glycerine initiated polyether polyol having a hydroxyl value of about 53 to about 57 mg KOH/gram.

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17. The method of claim 12 wherein the amount of sucrose based polyol is about 50 to about 62% by weight, the amount of toluene diamine based polyether polyol is about 13 to about 35 % by weight, and the amount of diaminodiphenylmethane based polyol is about 12 to about 20 %, all amounts by weight based on total weight of isocyanate-reactive compounds, and the blowing agent is cyclopentane.

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18. The method of claim 14 further comprising a physical blowing agent selected from the group consisting of dialkyl ethers, alkyl alkanoates, aliphatic hydrofluorocarbons, cycloaliphatic hydrofluorocarbons, hydrochlorofluorocarbons,

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chlorofluorocarbons, hydrochlorocarbons, fluorine-containing ethers, water and carbon dioxide.

19. The method of claim 14 further comprising a catalyst selected from the group consisting of

5 pentamethyldiethylenetriamine, dimethyl cyclohexyl amine, 1,3,5-tris(3-(dimethylamino)propyl) hexahydro-s-triazine, tin(II) acetate, tin(II) octanoate, tin(II) ethylhexanoate and tin(II) laurate, dibutyltin diacetate, dibutyltin dilaurate, dibutyltin maleate and dioctyltin diacetate.

10 20. A method of producing a polyurethane foam comprising reacting a polyisocyanate with an isocyanate reaction system having improved capacity for solubilizing a hydrocarbon blowing agent wherein the reaction system comprises

15 about 41.0 parts of a sucrose based polyether polyol having a hydroxyl number of about 420 to about 480 mg KOH/gram,

about 13.6 parts of a diaminodiphenylmethane based polyether polyol having 295 to about 325 mg KOH/gram,

20 about 23.9 parts of a toluene diamine based polyol having a hydroxyl number of about 375 to about 405 mg KOH/gram,

about 3.4 parts of a glycerine initiated polyol having a hydroxyl number of about 53 to 57 mg KOH/gram,

about 1.8 parts of a silicone surfactant,

25 about 1.2 parts of pentamethyldiethylenetriamine, about 0.5 parts 1,3,5-tris(3-(dimethylamino)propyl) hexahydro-s-triazine,

about 1.3 parts water, and

about 13.3 parts cyclopentane.

30 21. The reaction system of claim 9 wherein the catalyst is selected from the group consisting of pentamethyldiethylenetriamine, dimethyl cyclohexyl amine, and 1,3,5-tris(3-(dimethylamino)propyl) hexahydro-s-triazine.

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22. The method of claim 19 wherein the catalyst is selected from the group consisting of pentamethyldiethylenetriamine, and dimethyl cyclohexyl amine and 1,3,5-tris(3-(dimethylamino)propyl) hexahydro-s-triazine.

5 Claim 23. An isocyanate reactive composition having improved capacity for solubilizing hydrocarbon blowing agents comprising

a) a mixture containing

10 a1) a sucrose based polyether polyol having a hydroxyl number of about 100 to about 650 mg KOH/gram and a toluene diamine based polyether polyol having a hydroxyl number of about 100 to about 600 mg KOH/gram, said sucrose based polyether polyol and toluene diamine polyether

15 polyol being present in a ratio of about 3.75/1.0 to a ratio of about 1.55/1.0,

a2) a diaminodiphenylmethane based polyether polyol, and

20 a3) one or more low functionality polyols having functionalities from 2 to 3,

b) water in an amount greater than 0.65% by weight based on the total weight of mixture a), and optionally,

25 c) blowing agents, and

d) catalysts.

Claim 24. The isocyanate reactive composition of claim 23 wherein the sucrose based polyether polyol has a functionality of about 4.2 to 4.8 and the toluene diamine based polyether

30 polyol has a functionality of about 3.7 to about 4.0.

Claim 25. The isocyanate composition of claim 23, further comprising a glycerine initiated polyether polyol having a hydroxyl number of about 45 to about 70 mg KOH/gram.

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Claim 26. A method of producing a polyurethane foam comprising reacting an organic polyisocyanate with a polyfunctional isocyanate reactive composition of claim 1.

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Claim 27. The method of claim 26 further comprising a glycerine initiated polyether polyol having a hydroxyl number of about 45 to about 70 mg KOH/gram.

10

Claim 28. A method of producing a polyurethane foam comprising reacting an organic polyisocyanate with the polyfunctional isocyanate reactive composition of claim 24

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/16659

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G18/48 C08J9/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08G C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	US 5 547 998 A (MULLINS JAMES A ET AL) 20 August 1996 (1996-08-20) column 3, line 21 -column 3, line 63 column 18, line 6 -column 18, line 17 example 1; table 1 table 3 claims 1,2,8,12	1-5, 9, 11-15
X	US 4 469 822 A (STOLZ THEODORE O ET AL) 4 September 1984 (1984-09-04) table 1 examples 1,5	1-3

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

International Application No.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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